

## LA-UR-19-21570

Approved for public release; distribution is unlimited.

Title: Colloid-Facilitated Transport: Studies Related to CFM Project at GTS

Author(s): Boukhalfa, Hakim  
Reimus, Paul

Intended for: Program review

Issued: 2019-02-25

---

**Disclaimer:**

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.



# Colloid-Facilitated Transport: Studies Related to CFM Project at GTS

U.S. Nuclear Waste Technical Review Board Spring Meeting  
Feb 26, 2019  
Las Vegas, Nevada

Hakim Boukhalfa, Los Alamos National Laboratory  
Paul Reimus, Los Alamos National Laboratory (Retired)

# Colloid-Facilitated Transport Team

## **Los Alamos National Laboratory**

Katherine Telfeyan, Paul W. Reimus, Hakim Boukhalfa,  
S. Doug Ware



## **Sandia National Laboratories**

Wang, Yifeng



## **Lawrence Livermore National Laboratory (LLNL)**

Mavrik Zavarin



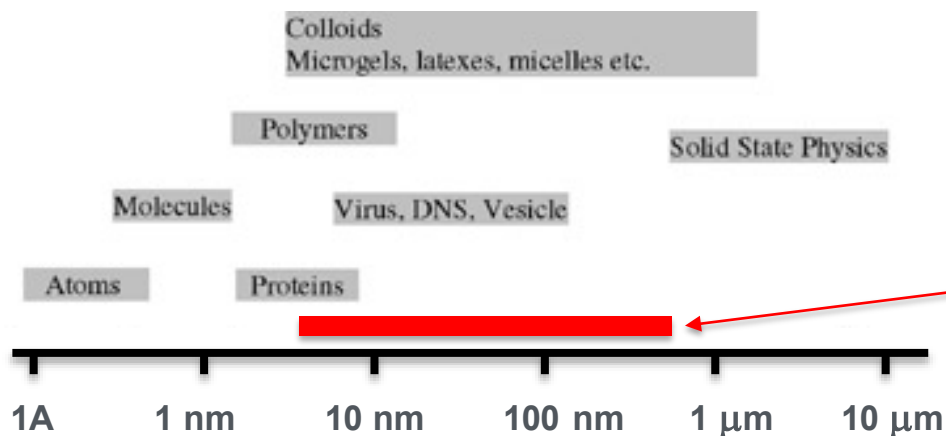
## **Department of Energy\***

Jay Jones, Prasad Nair

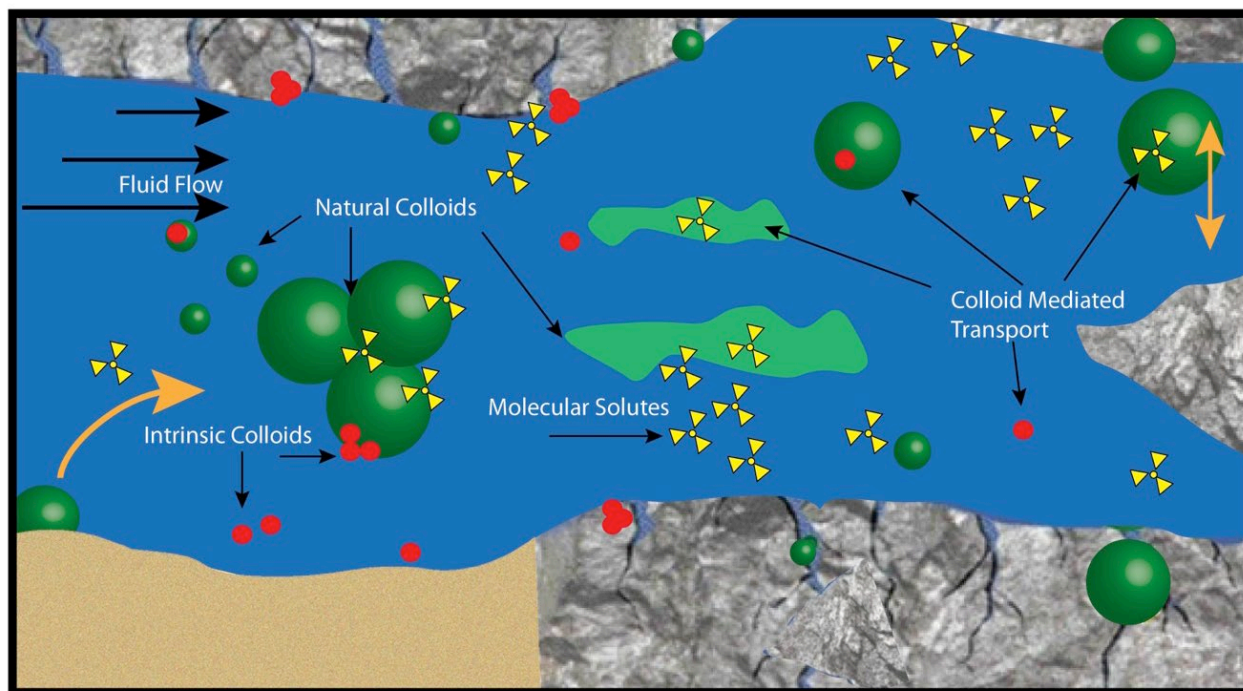
\*During the time of formal DOE participation in CFM Project (2013-2015)

# Colloid-Facilitated Transport (CFT) of Radionuclides

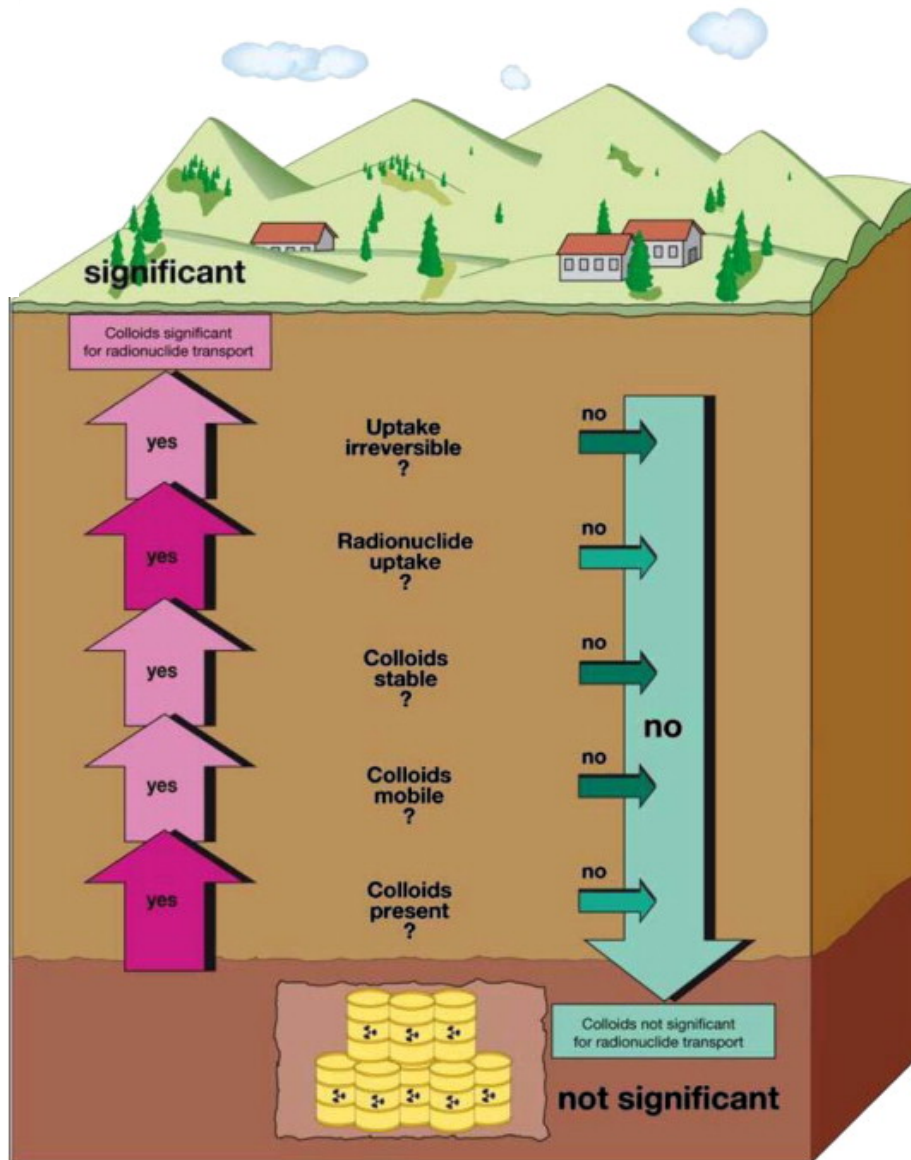
## Colloids



## Colloid-Facilitated Transport of Solutes



# The “CFT Ladder”



In Words:

For CFT to be a problem, you need stable colloids that are capable of migrating long distances, AND you need radionuclides to be very strongly associated with these colloids

# CFM (Colloids Formation and Migration) Project Overview

## Structure of the CFM Project

### Laboratory studies

Colloid-Rn interaction  
Colloid Generation  
Field test analysis

- Colloid generation
- Colloid transport/retardation and stability
- Radionuclide association
- Bentonite intercomparison (MX-80, Febex, Kunigel)

### Field experiments

In situ test: formation & Migration tests with colloids, homologues, Rn tracers

- Site characterization and site preparation
- Assessing the advective travel times
- Analyzing the recovered tracer mass
- Estimating dispersion parameters in the shear zone flow fields

### Modelling studies

Solute, colloid and associated Rn transport  
Colloid generation

- Supporting the in-situ tests
- Initiating performance-assessment relevant studies on colloid generation and on colloid-facilitated radionuclide transport

# Grimsel Test Site



Grimsel Test Site

Location : Grimsel Pass (Canton Bern)

Elevation : 1730 m asl

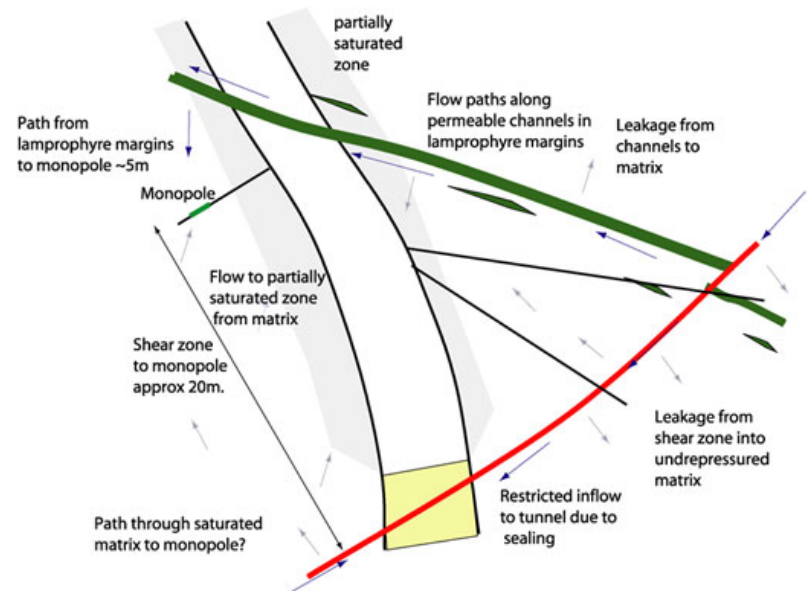
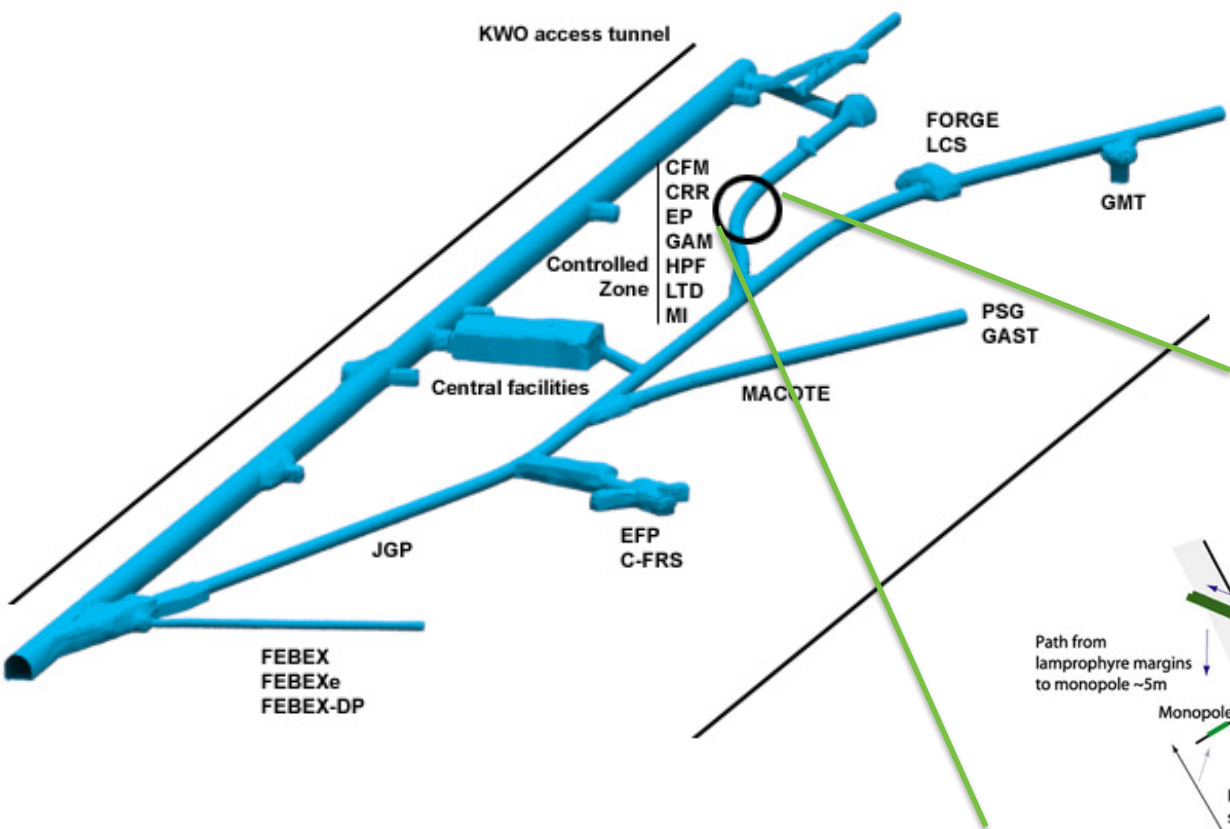
Overburden : 450 m

Constructed : 1983



(1) Grimsel Test Site, (2) Rättrichsbodensee,  
(3) Grimselsee, and (4) Juchlistock

# The GTS Underground Facilities



**CFM in-situ experiment**

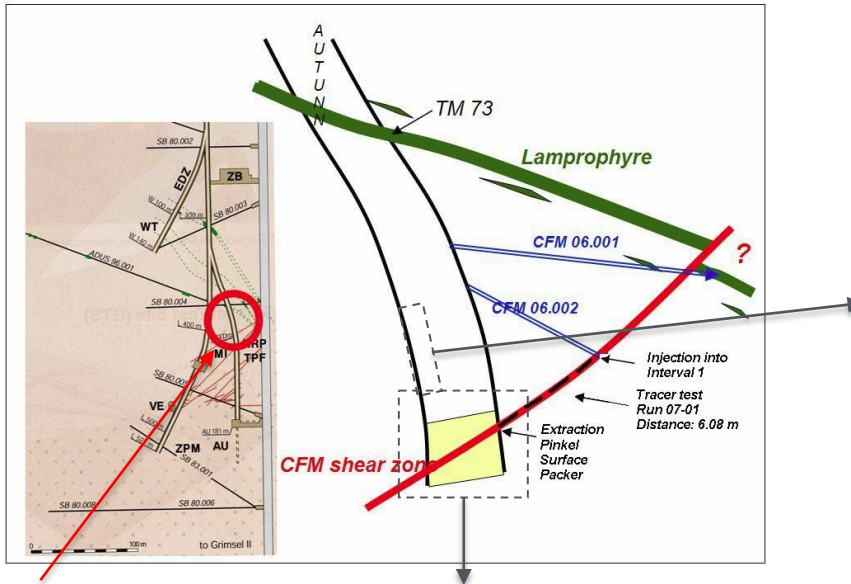
# CFM (Colloids Formation and Migration) Project Overview

- CFM began in 2004 (preceded by CRR, Colloid and Radionuclide Retardation Project, 1998-2003)
- U.S. was formal partner in 2013-2015, with informal involvement since 2006
- Focus has always been on bentonite colloids in fractured crystalline media (a granodiorite at GTS)
  - Relevant Scenario: Waste package breach allows radionuclides to sorb onto bentonite backfill, which subsequently erodes into flowing fractures, carrying radionuclides away on colloids
- Distance Scales: ~2 – 6 meters
- Time Scales: 1 – 60 hours (mean residence times), with general progression of increasing time scales
- RN-doped bentonite plug emplacement in 2015

# CFM Project Testbed

## Hydraulic Isolation and Control of Shear Zone Inflow via 3.5-m Diameter “Packer”

Plan View of Testing Area

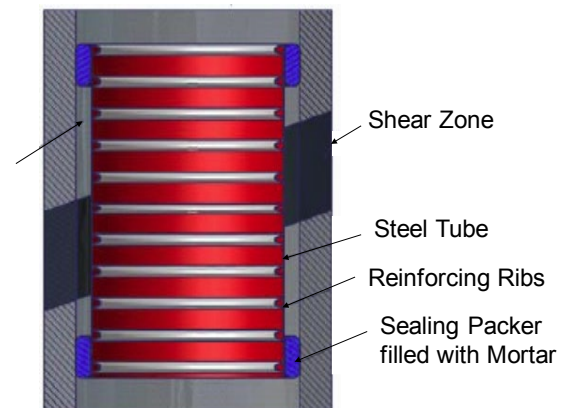
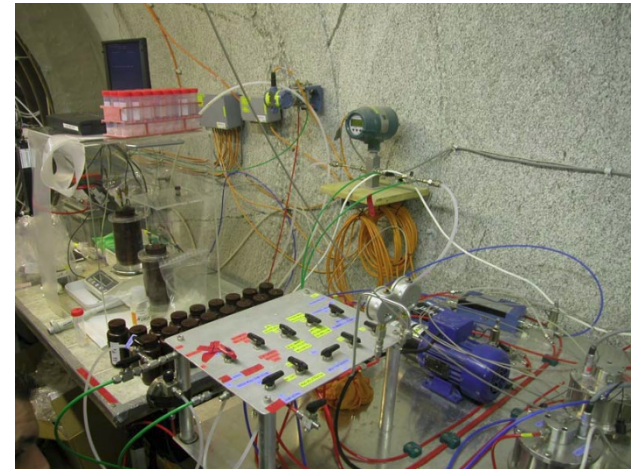


Radiological  
Control Area

Pinkel Surface Packer

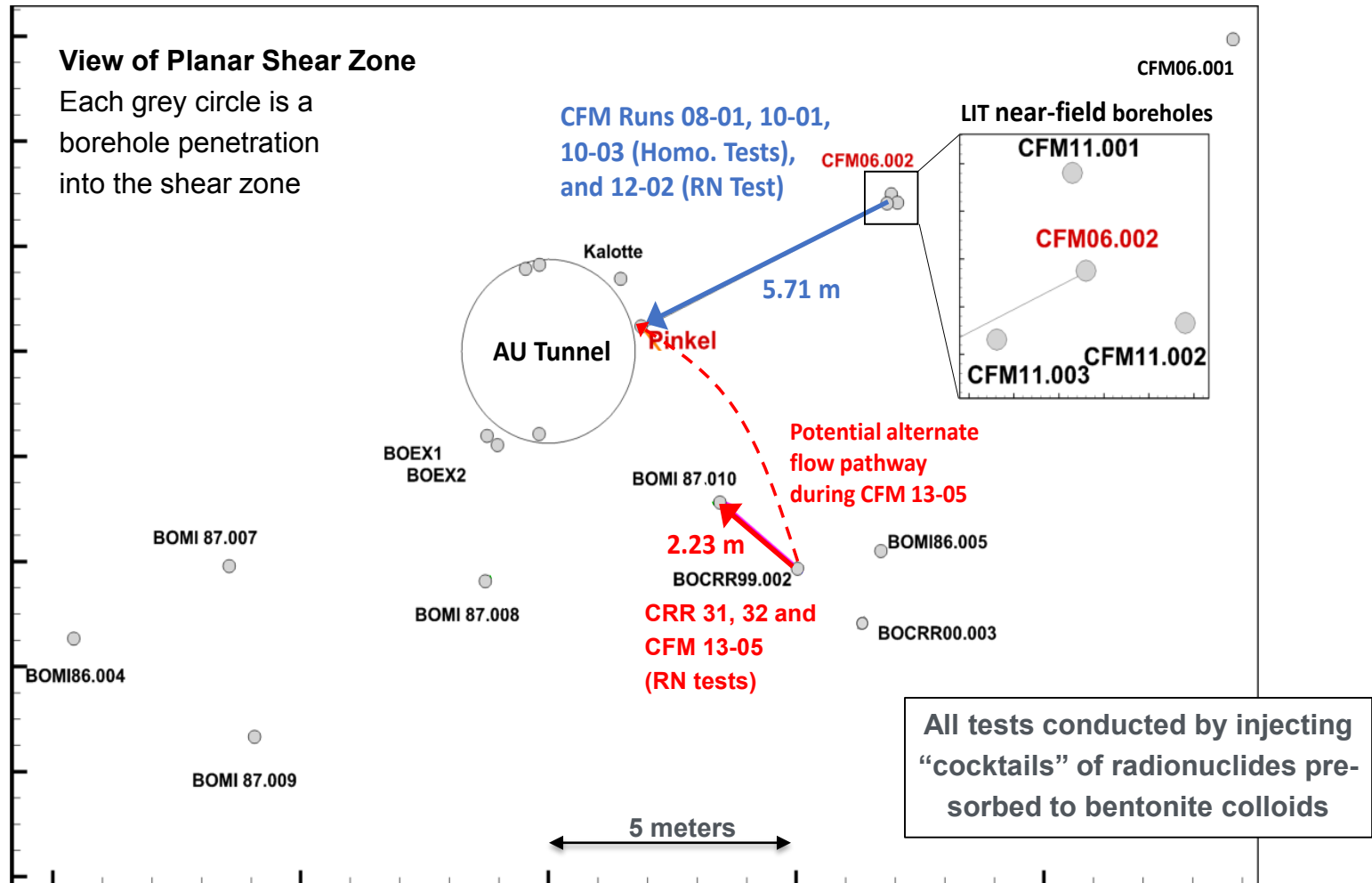


Testing Control and Data Acquisition System



# Colloid-Facilitated Transport Tests (2002-2013)

6 CFT Tests: 3 with tri- and tetravalent “homologues”, and 3 with radionuclides  
(also one radionuclide test without colloids, CRR 31)

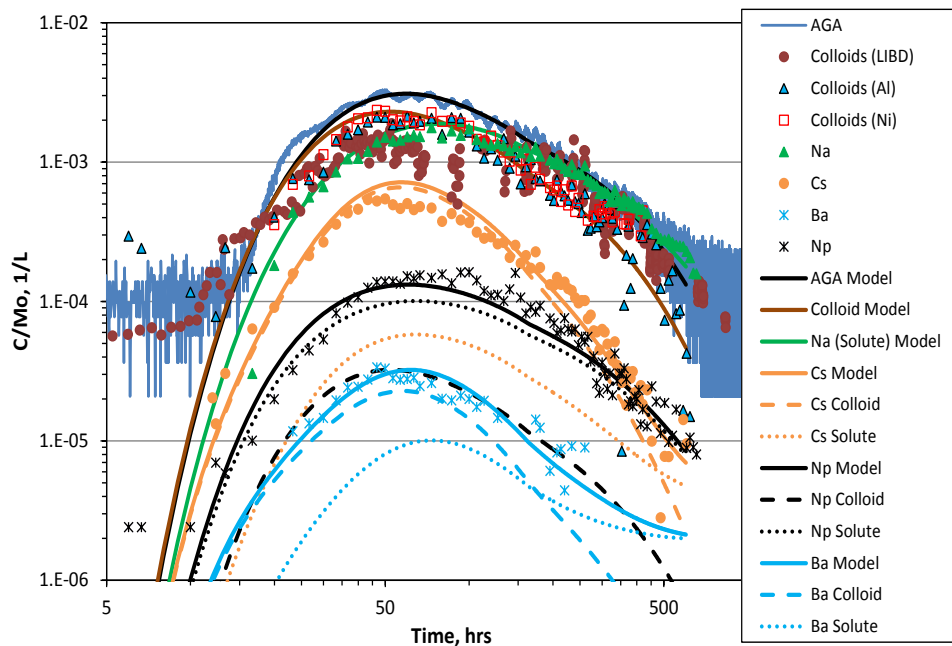


# Example of Model Interpretations (CFM Test 12-02)

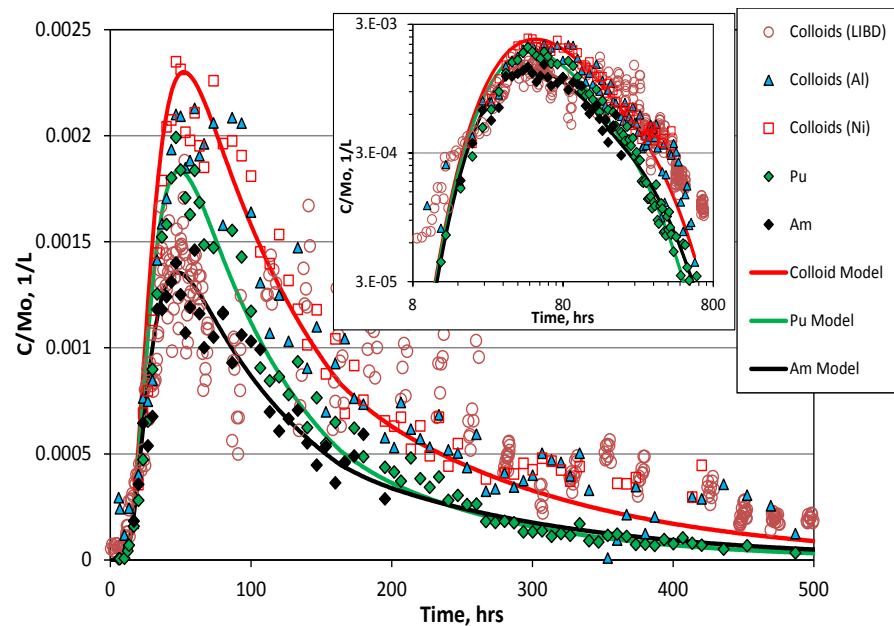
## Modeling Approach:

- Model Conservative Tracer First (Amino-G Acid, or AGA)
- Then Model Colloids Using Filtration Parameters Coupled with Conservative Transport
  - Account for lower colloid recovery relative to conservative tracer by filtration processes
- Then Model Radionuclides using Sorption/Desorption Parameters Coupled with Colloid Transport
  - Account for lower radionuclide recovery relative to colloids by RN desorption from colloids

## Conservative Tracer (AGA), Colloids, and Selected Radionuclides

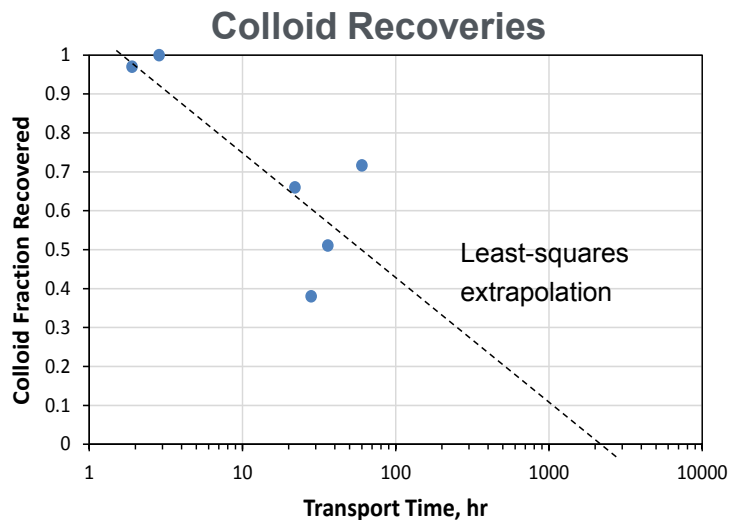
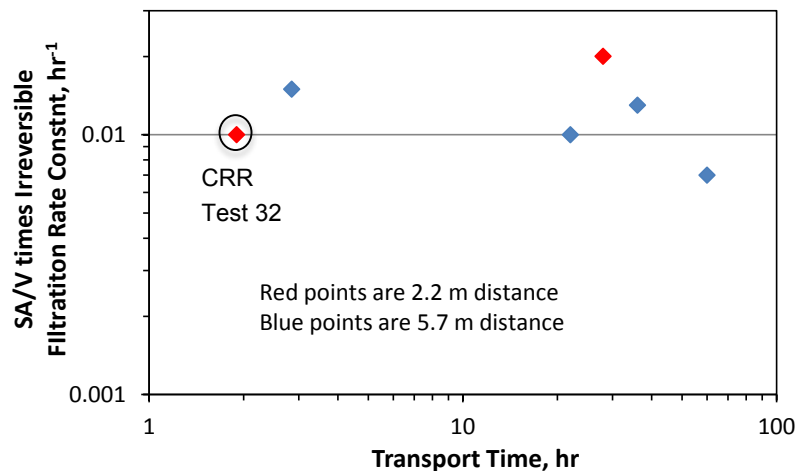


## Colloids, Pu, and Am



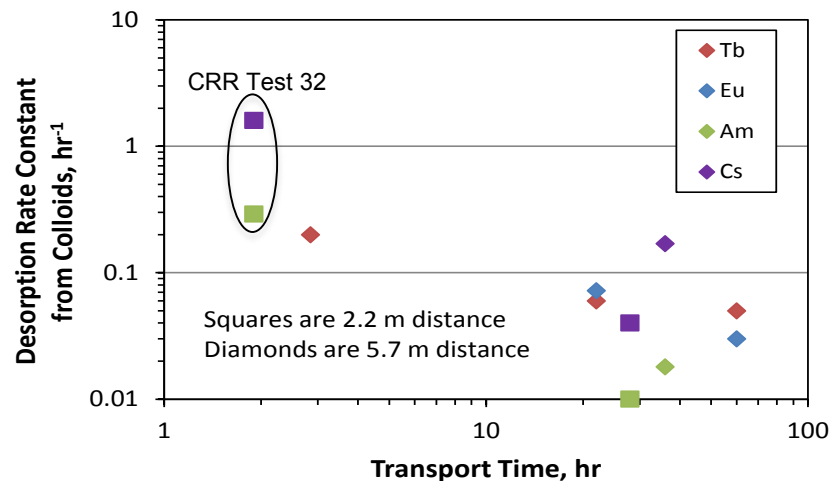
# Summary of 2002-2013 Results

## Bentonite Colloid Filtration Rate Constants

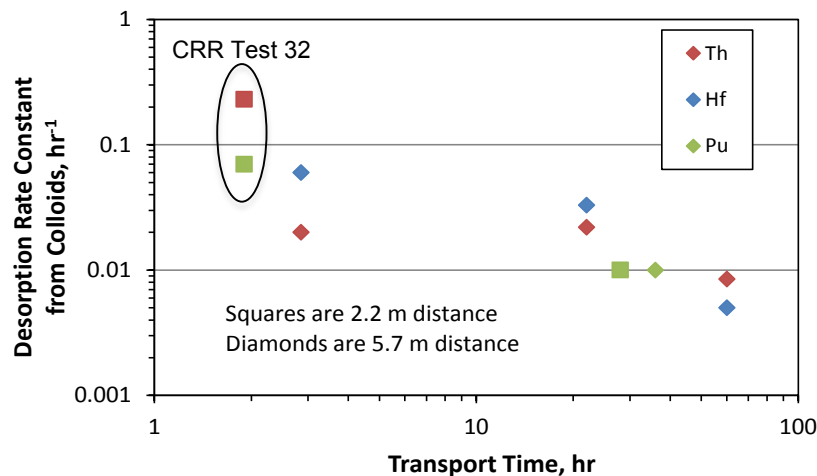


## RN/Homologue Desorption Rate Constants

### Trivalents and Cesium

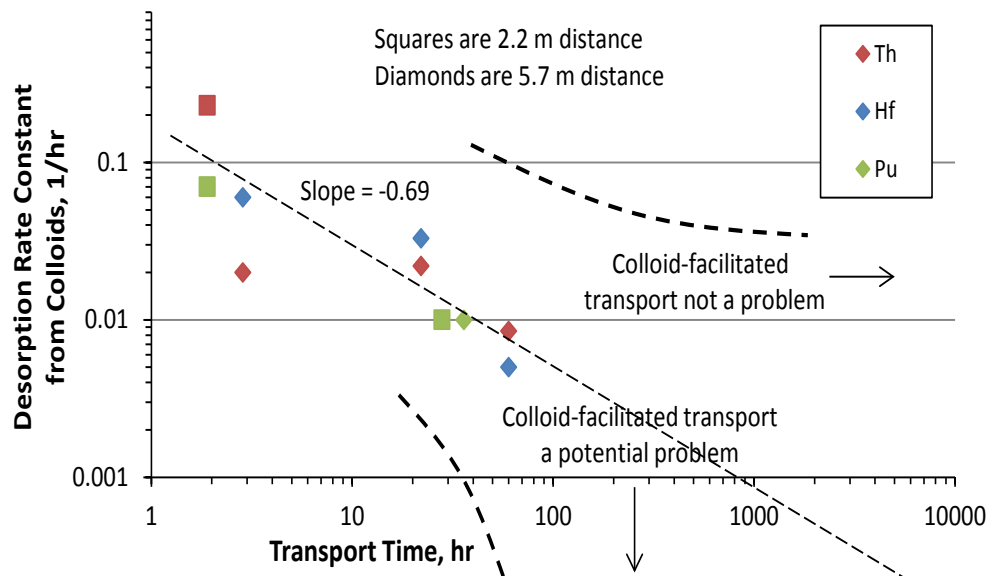


### Tetravalents



# Upscaling Questions

## Can a Simple Extrapolation be Applied?

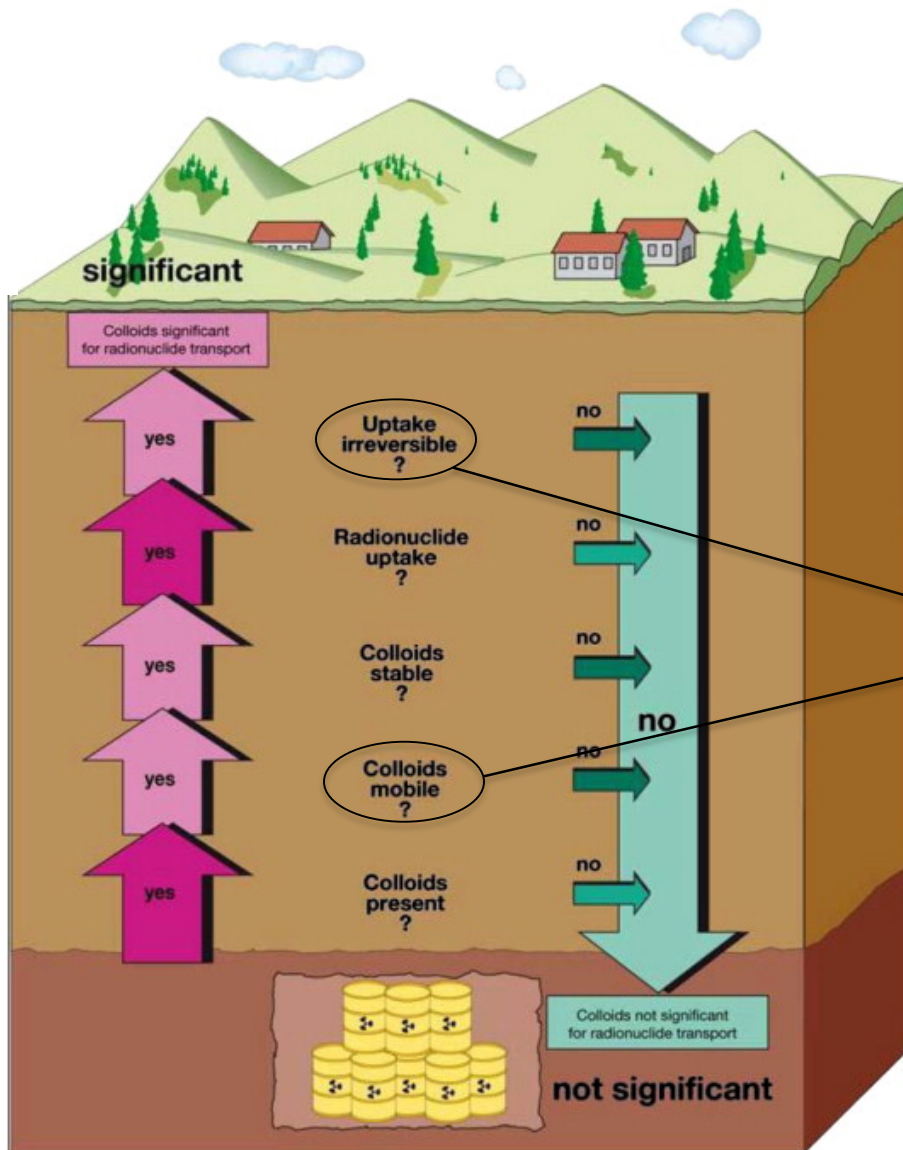


This plot is not interpreted as a literal decrease in desorption rate constants with increasing time scale, but rather as a revelation of stronger and stronger sorption sites (with smaller desorption rate constants) as time scales increase.

The key question is: Are there any sorption sites with slow enough desorption rates to be effectively irreversible over repository time and distance scales?

And if so, are there any colloids that will remain mobile over these time/distance scales?

# CFM and the “CFT Ladder”



## CFM answers:

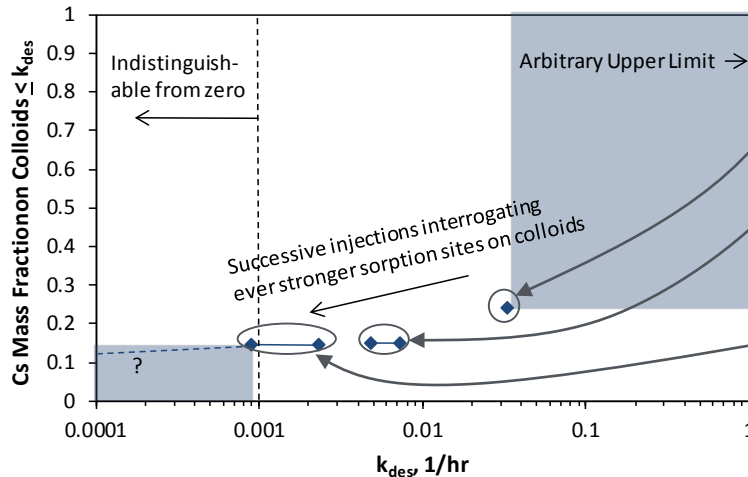
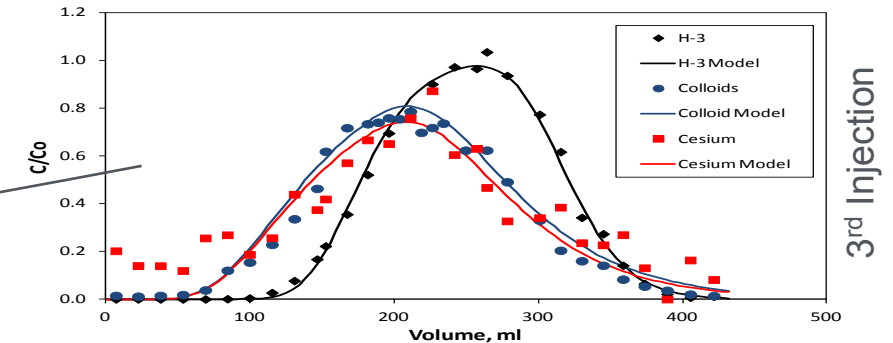
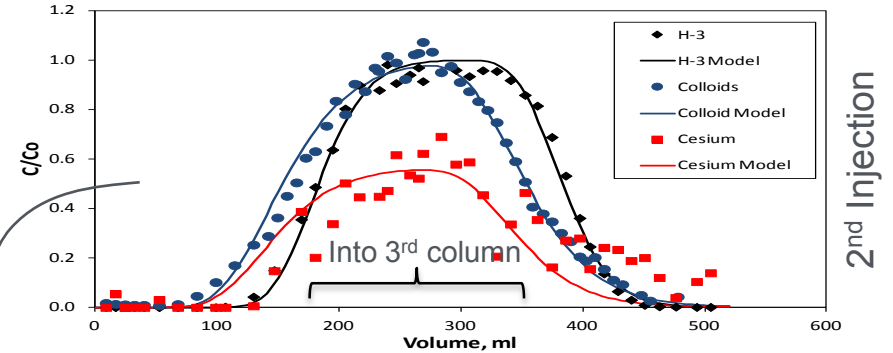
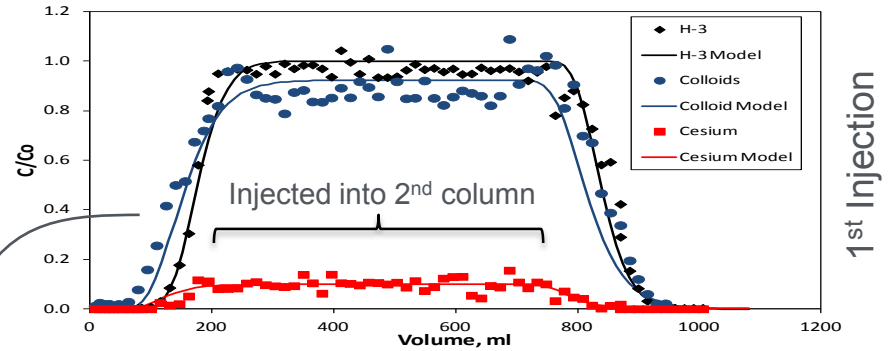
Yes, for up to 100 hrs and 6 meters in case of bentonite colloids in groundwater with ~0.7 mM ionic strength, but extrapolation to longer time and distance scales is a big uncertainty

# Recent Approach in Lab Testing: Cs Associated with NNSS Colloids

Columns

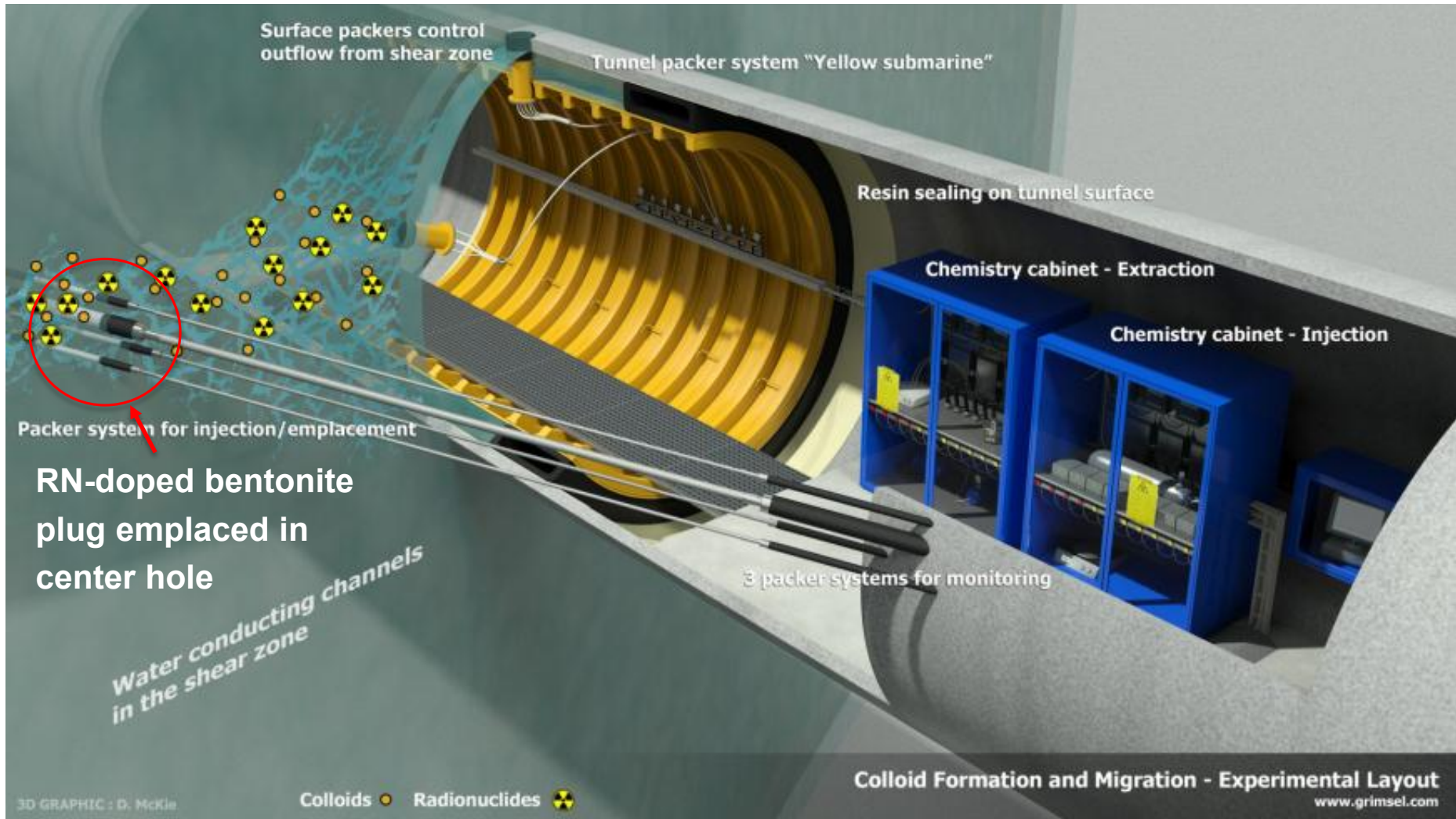


Repeat Injections of Cavity Water (~48-hr Residence Time)



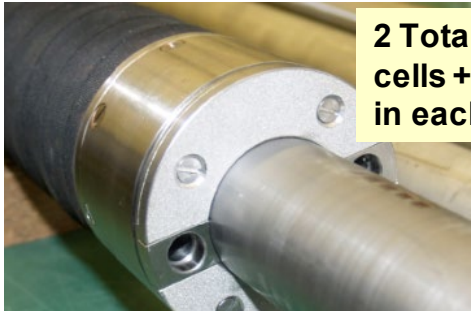
Each successive injection interrogates stronger Cs sorption sites on colloids

# CFM Long-Term In-Situ Test (LIT): 2015-present



Shear-zone flow kept the same as in CFM 12-02 test

# RN-doped bentonite emplacement details

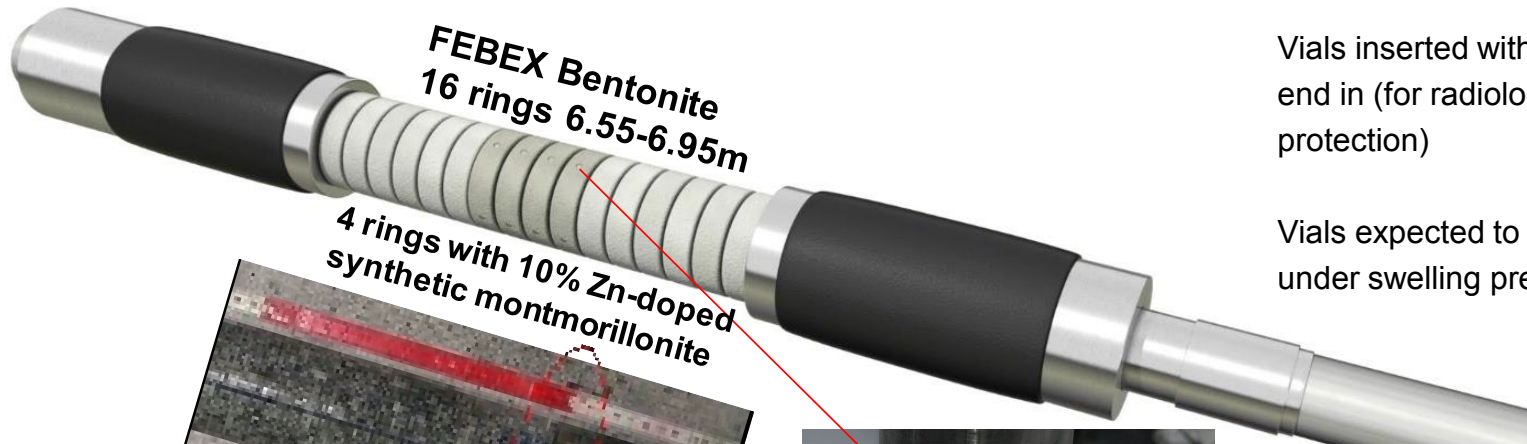


2 Total Pressure cells + piezometer in each packer face



Precompact rings of FEBEX bentonite:

- Outer diameter: 82mm
- Inner diameter: 43mm
- Dry density: 1.65Mg/m<sup>3</sup>
- Gravimetric water content: ~14%

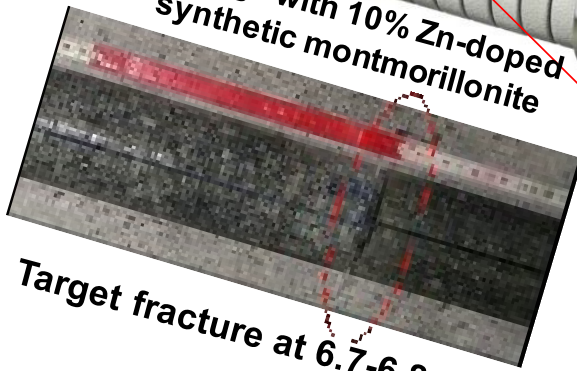


FEBEX Bentonite  
16 rings 6.55-6.95m

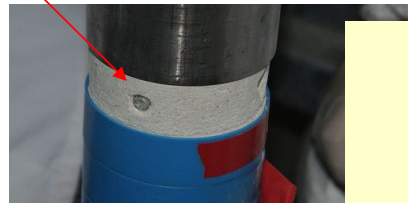
4 rings with 10% Zn-doped synthetic montmorillonite

Vials inserted with open end in (for radiological protection)

Vials expected to break under swelling pressure



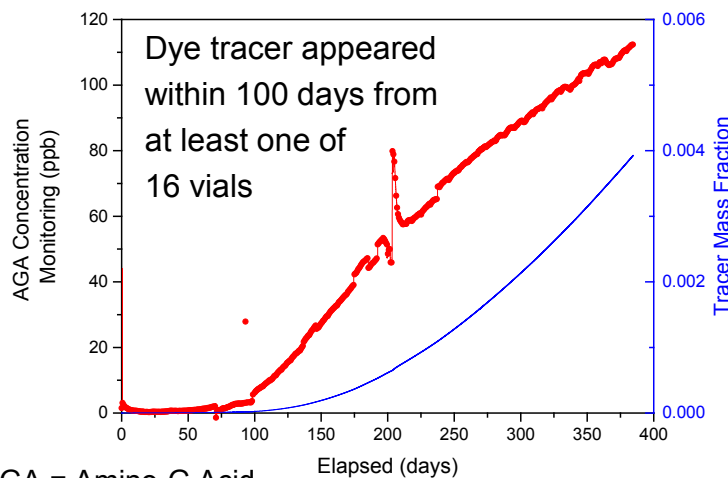
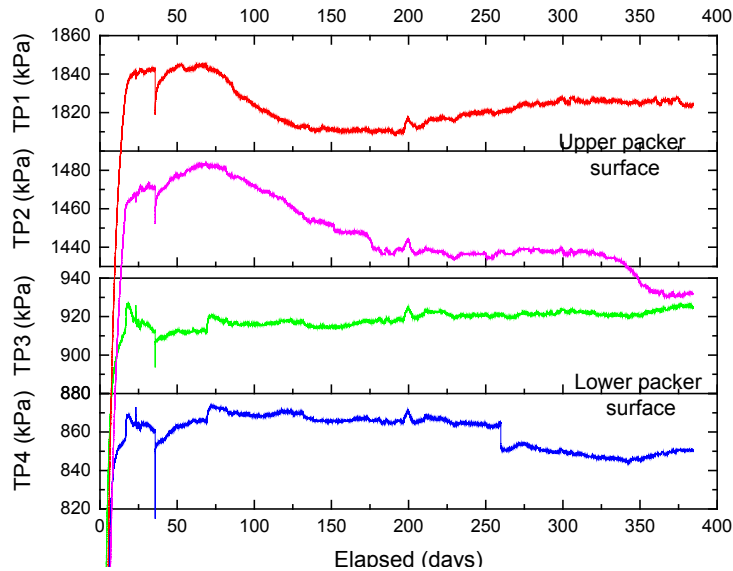
Target fracture at 6.7-6.8m



16 Vials

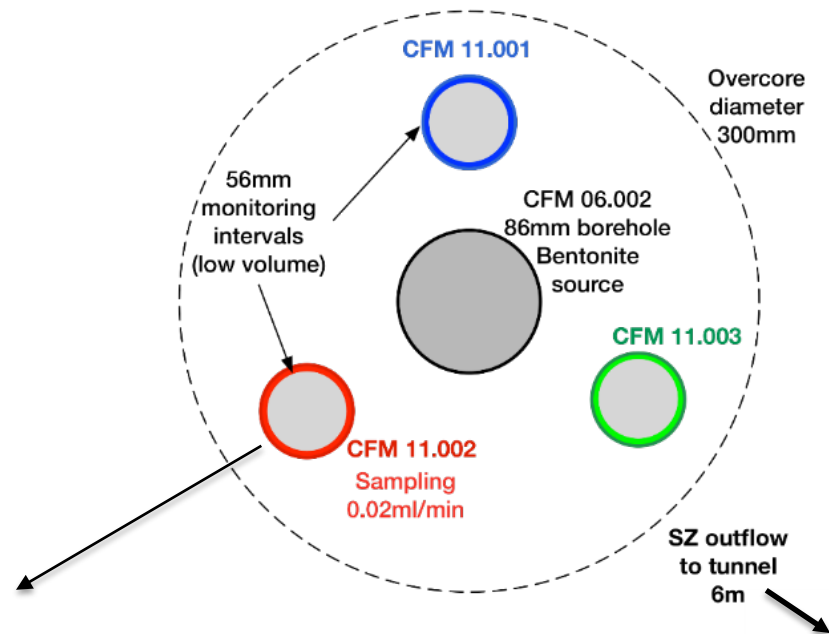
# First ~400 days of monitoring in near-field boreholes

## Bentonite saturated and swelled very quickly



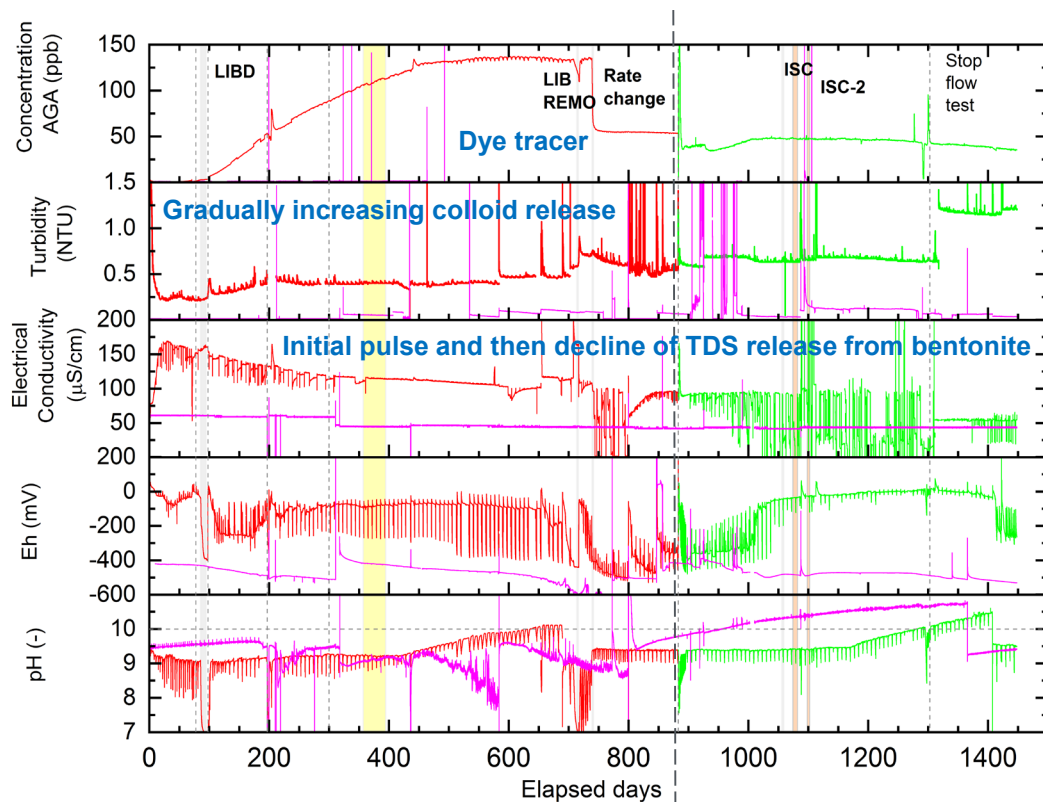
AGA = Amino-G Acid

## Overcoring (excavation) initiated in December 2018

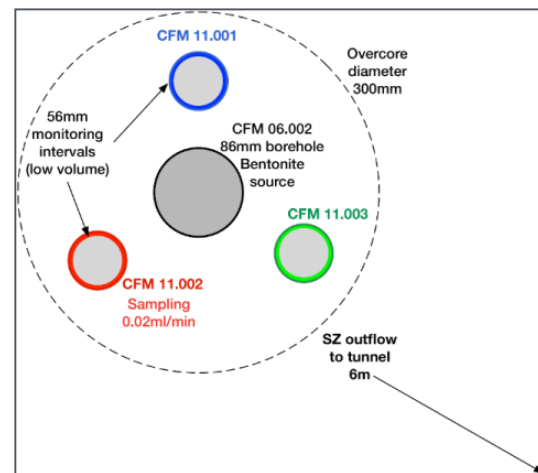


# Longer-Term (~4-yr) Results

- Only conservative tracer and minor colloid breakthroughs in monitoring holes (6-7 cm away)
- However, very small concentrations (ppq) of  $^{99}\text{Tc}$  are being detected by AMS in monitoring hole
- Almost imperceptible concentrations of conservative tracer and colloids at tunnel wall (~6 m away)
- No actinides detected anywhere



Switch from red to green monitoring hole (882 days)



More detailed information expected from overcoring and post-mortem

DOE will get delayed information because of withdrawal from formal CFM partnership in 2015

# Summary of Knowledge Gained from CFM Participation

- Insights have been gained as to how to obtain defensible answers to predict radionuclide transport in fractured granites. However, site specific studies still need to be performed to gain confidence in the prediction
- The CFT ladder should be applied to evaluate the potential for enhanced transport with colloids, but most indications are that only very small fractions of strongly-sorbing radionuclides will be capable of CFT over repository time and distance scales
- CFT requires very slow desorption from colloids AND very slow filtration of the RN-bearing colloids (relative to time scales of interest)
- Interrogating such slow processes is a challenge, especially if they are associated with a very small fraction of colloids or very small fraction of sorption sites on colloids (or both)
- Intuitively, one might expect that stable colloids generated from waste-form degradation that have radionuclides incorporated into their structure (as opposed to a sorption association) might pose the biggest risk

# Summary of Knowledge Gained from CFM Participation (2)

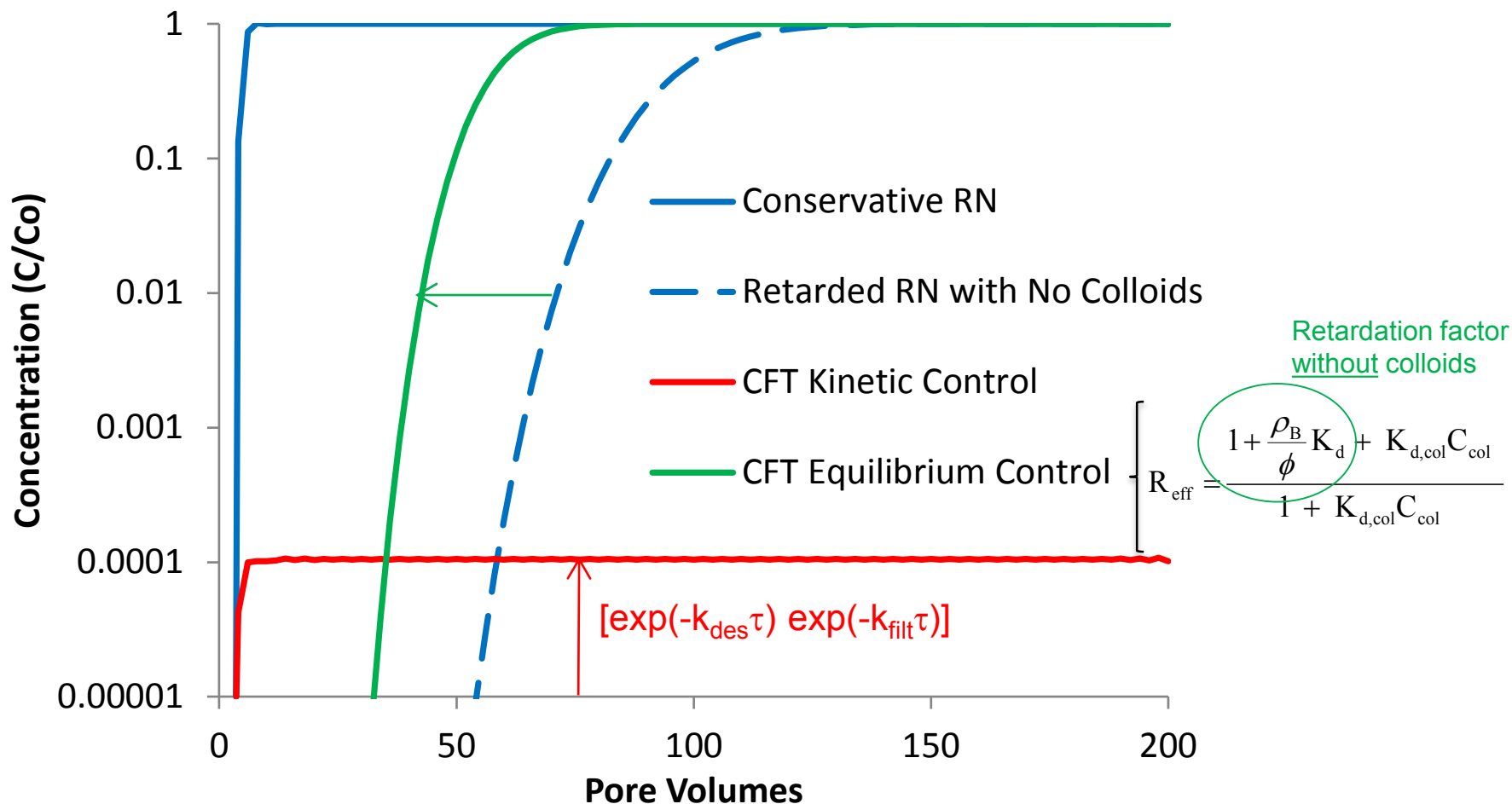
- Experiments have informed generic modeling approach, including GDSA
- Experiments have provided insights into how experimental designs can be tailored and improved to address site-specific and scenario-specific issues
- Different host rocks, EBS vs. natural system, and DPC concept can all, in principle, be addressed via different parameterizations of the generic model, with the understanding that parameterizations must be developed through site- and scenario-specific experimental testing

## Refer also to:

Colloid-Facilitated Radionuclide Transport: Current State of Knowledge from a Nuclear Waste Repository Risk Assessment Perspective, *FCRD-UFD-2016-000446*, August 2016.

Mathematical Basis and Test Cases for Colloid-Facilitated Radionuclide Transport Modeling in GDSA-PFLOTRAN, *SFWD-SFWST-2017-000117*, August 2017.

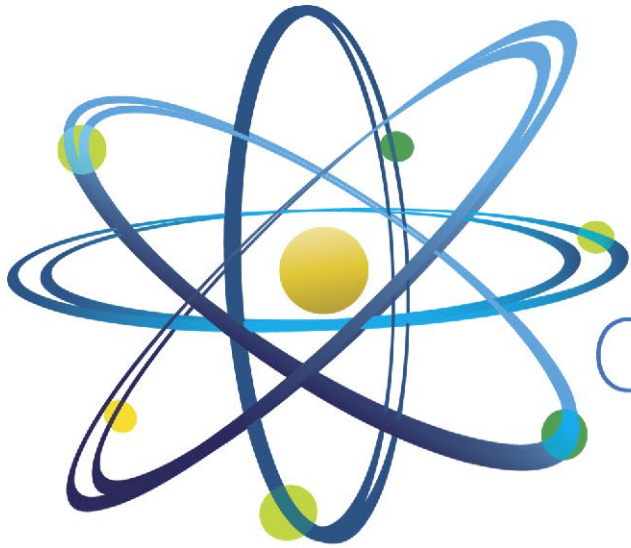
# Graphical Depiction of GDSA Approach



For complete model description, refer to:

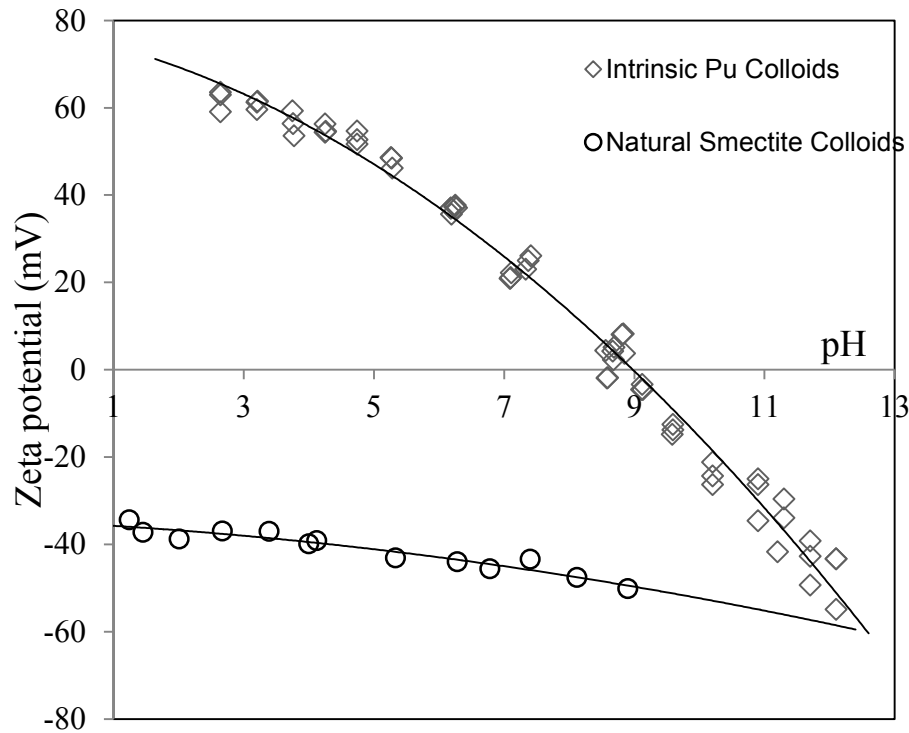
Mathematical Basis and Test Cases for Colloid-Facilitated Radionuclide Transport Modeling in GDSA-PFLOTTRAN, *SFWD-SFWST-2017-000117*, August 2017.

# Questions?

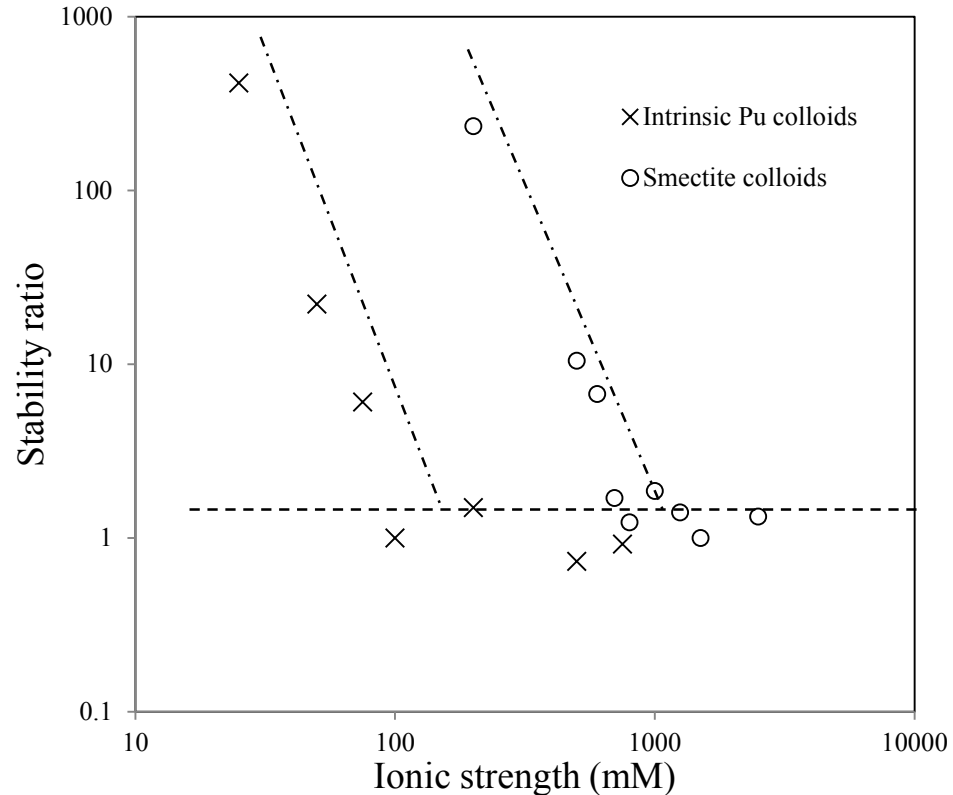


Clean. **Reliable. Nuclear.**

# $\zeta$ -potential of Pu(IV) intrinsic colloids and smectite colloids and the relative stability of their suspensions



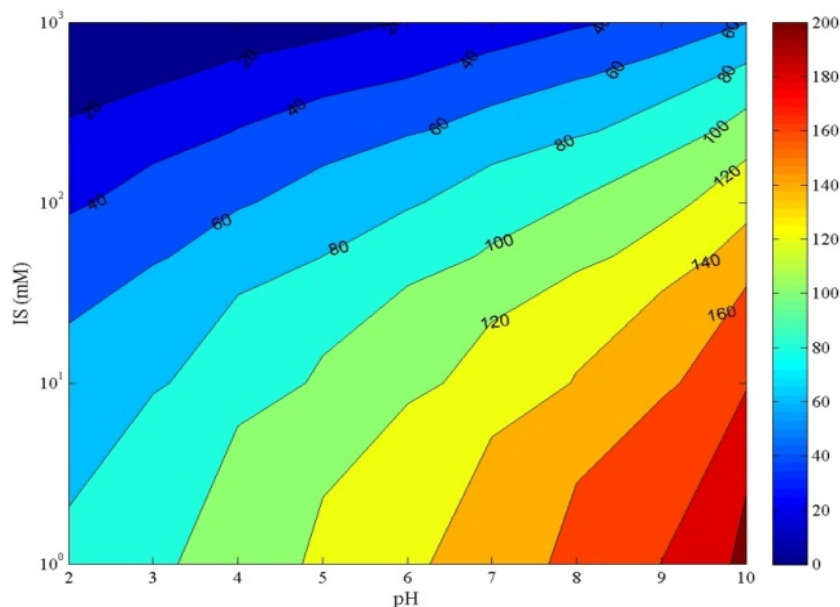
The opposite  $\zeta$ -potentials of intrinsic Pu(IV) colloids and smectite colloids below pH 8.6 indicate high electrostatic attraction between the two colloids. This result indicates that Pu(IV) colloids will likely attach smectite colloids under pH conditions typical to the subsurface environment.



Intrinsic Pu(IV) colloids are relatively stable (i.e., undergo slow or no aggregation compared to the diffusion-limited aggregation rate) only at very low salt concentrations (10 mM and 25 mM). They undergo rapid aggregation at higher ionic strength

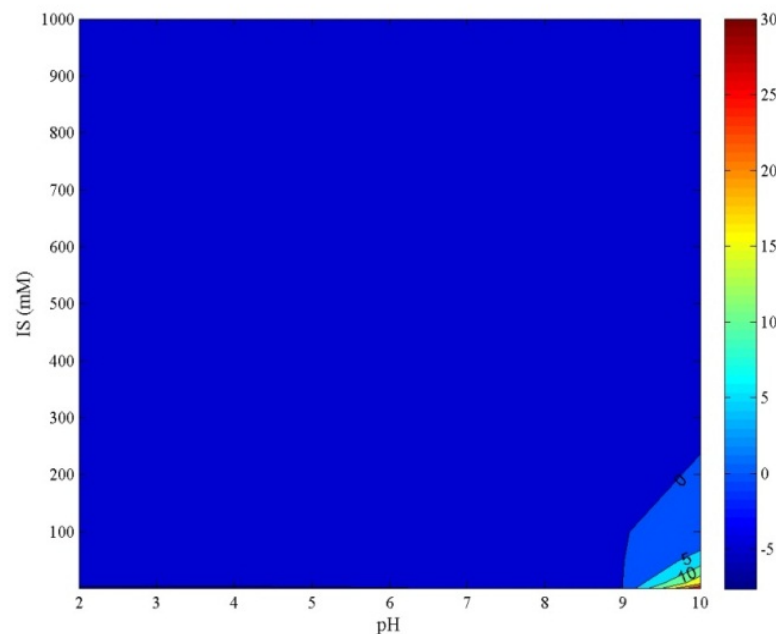
# Energy barrier contour maps of smectite and Pu(IV) intrinsic colloids surface interactions

Smectite colloids-surface interactions



The energy barrier is significantly high between smectite colloids and surrounding wall surfaces over the entire pH and the range, of ionic strengths

Pu(IV) colloids-surface interactions



The energy barrier between Pu(IV) colloids and the surrounding stationary wall surfaces does not exceed  $\sim 2 kT$  across the same range of ionic strength and pH.